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The Determination of the Time between Excitation
and Emission for Certain Fluorescent Solids.

By

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The Determination of the Time between Excitation
and Emission for Certain Fluorescent Solids.

Introduction.

It has been shown recently by Professor H.W.Wood* that some fluorescent substances remain dark during a definite period of excitation. He showed, in other words, that the exciting energy was imprisoned for a short, but definite and measurable interval of time within the fluorescent substance. In the case of mercury vapor, $1/15000$ second was obtained by him as the intervening period between the beginning of the process and the emission of the light. Similar observations made with barium-platino-cyanide indicated that not only was this interval of time less than $1/400000$ second, but, furthermore that, the total duration of the phosphorescence, i.e. the continued process of emission of light energy after the exciting incident energy ceases to fall upon the fluorescent substance, was also very short.

It was evident that the period of darkness for barium platino cyanide was outside the range of the synchrono-phosphoscope method employed by Professor Wood, and he suggested that the method of Abraham and Lemoine might lend itself to an accurate determination of the period in question.

The method of Abraham and Lemoine makes use of the double refractive property of liquids when subjected to an electrostatic field.

* Proc. Roy. Soc. A. vol. 99, 362, 1921.

A condenser formed by immersing two metal plates in a liquid such as carbon bisulphide or nitrobenzene, is allowed to discharge through a spark gap. A Nicol prism is placed between the spark gap and the condenser, and, if the spark is viewed through the space between the condenser plates, it is impossible to extinguish the light by a second Nicol held close to the eye, unless the path over which the light must travel is increased in some such way as reflection in a distant mirror. In the latter case a position of the mirror can be found for which the light from the spark can be extinguished by the second or analysing Nicol.

It is evident from this that the double refraction of the liquid under these conditions varies in degree with the time. This circumstance might be employed to measure the time which expires between the instant of occurrence of the spark and the instant fluorescent light bursts from some substance excited by the spark. For if the fluorescent light were reflected in the mirror, a position of the latter could be found for which the fluorescent light could be entirely extinguished by the analysing Nicol. The distance between this position and the corresponding position when the light from the spark could just be entirely extinguished, when divided by the velocity of light, would give the time the fluorescent substance remains dark.

Description of Apparatus.

For the particular problem at hand, however, it was found advantageous to elaborate on the simple arrangement and method just described by introducing a double image prism into the optical path

of the light between the condenser and analysing Nicol. The final electrical circuit and optical arrangement employed were as shown in Figure 1, and are very similar to those proposed by Lord Rayleigh*.

The spark gap P was connected through a resistance R to the condenser C containing nitrobenzene and which shall be referred to as the Kerr cell. The latter alone gave a poor spark, but by connecting another condenser A, a Leyden jar, in parallel with the first circuit, as shown in the figure, a fine bright spark was obtained. The condensers A and K were charged intermittently by an ordinary spark coil U with a twelve volt storage battery connected to the primary, and were allowed to discharge through the spark. N_1 is the polarizing Nicol and N_2 the analysing Nicol. D is the double image prism placed between the Kerr cell K and N_2 , and was so oriented as to give only one image of the narrow slit S when K was disconnected from the electrical circuit. The analysing Nicol N_2 was then turned to the position of extinction of this image. Call this the zero position of N_2 . Replacing the Kerr cell in the electrical circuit caused the restoration of one of the images, namely the one whose plane of vibration was parallel to the short diagonal of the analysing Nicol. Turning N_2 through a small angle restored the other image, and two positions of N_2 , obtained by turning it clockwise in one case and counter-clockwise in the other case, could be found at which the intensities of the two images appeared the same. The angles, α , through which N_2 must be turned to arrive at these positions, when

* Scientific Papers. Vol. V, p. 190.

opposite in direction, are equal in value. If, instead of illuminating the slit S by the spark directly the light is first made parallel by a lens L, reflected in a mirror M, and brought to a focus again either by the same lens L, or another, and the light from this final image employed to illuminate the slit S, it is found that the angle α is different for different positions of the mirror M. Curves I and II, figure 2, plotted with $2\pi a$ as abscissae and distance d between the mirror and spark as ordinates show typically the variation referred to above, with two different values of the resistance R.

The plates of the Kerr condenser were 18.05 x 2.9 centimeters and were two millimeters apart. Therefore the capacity

$$K = \frac{A}{4\pi d} = \frac{34}{48} \frac{2.9 \times 18.05}{2} = 447 \text{ centimeters} = 49.7 \times 10^{-11} \text{ farads}$$

The inductance, L, of the K-R-P circuit may be taken as approximately that of a circle of the same sized wire and of one foot diameter. This is calculated from the formula given by W.H. Nottage*: $L = 4\pi a (\log_e \frac{8a}{r} - 2)$ where a is the radius of the circle to the center of the wire, and r is the radius of the wire of circular section. The wire was number 18 S.W.G. The inductance of a foot diameter circle of this is 1073 centimeters. Taking 1100 centimeters as the value of L in the actual circuit employed it is found that K must be greater than $\frac{4L}{C} = 94.3$ ohms in order that the discharge of K be non-oscillatory. The resistance employed in most cases was one hundred ohms or greater.

Furthermore the time constant, KR, of the K-R-P circuit, i.e. the time required for the potential between the plates of K to fall to 36.8%

* W.H.Nottage. Calc. & Meas. of Ind. & Cap. p. 17

of its original value - if 300 ohms be the value of R, is $KR = 300.49.7 \cdot 10^{-11} = 1.49 \times 10^{-7}$ sec.

The period of the spark-Leyden, i.e. the A-P circuit

$$T = \frac{c L}{5.023 \times 10^6} = \frac{.0003 \times 1100}{5.023 \times 10^6} = 1.14 \times 10^{-7} \text{ sec.},$$

where C is the capacity in micro-farads and L is the inductance in centimeters. Here, as in the previous case, the inductance of the circuit is assumed approximately equal to that of a circle of one foot diameter. The period was also determined by comparison with that of the same circuit when the capacity of A was increased from its value .0003 microfarads to .00693 microfarads. With the latter capacity in the A-P circuit, photographs were taken of the spark reflected in a rapidly revolving mirror. These photographs showed clearly the alternate bright and dark regions. The distance between successive bright regions measured by the dividing engine was .0172 centimeters.

The angular velocity of the mirror was 161.7 revolutions per second; consequently the angular velocity of the rays was 323.4 revolutions per second. The focal length of the camera lens was 26.5 cm. Hence the velocity of the image across the photographic plate was $2\pi \cdot 26.5 \cdot 323.4 = 53847.6$ cm. per sec. From this the period of the spark was $2 \frac{.0172}{53848} = 6.16 \times 10^{-7}$ sec. Since the period is proportional to the square root of the capacity, the period, when the capacity A is .0003 microfarad, is $6.16 \times 10^{-7} \sqrt{\frac{.0003}{.00693}} = 1.25 \times 10^{-7}$ sec.

Theory.

We may now consider the electrical sequence of events of the circuits in Figure I and the resulting optical effects. The interrupter of the primary circuit of the induction coil C induces a high potential in the secondary, which in turn charges the condensers A and K. This charging process continues until the breakdown potential of the spark gap P is reached. At the occurrence of the spark P, an oscillatory discharge of A through P begins, while the discharge of K through the resistance R and P is non-oscillatory if, for the circuit K-R-P, $\frac{R^2}{4L^2} > \frac{1}{LK}$, where L is the inductance of the circuit and K the capacity of the Kerr condenser. This condition was maintained during the experiment.

The discharge of the Kerr cell through the resistance R and spark P may be represented analytically by the equation

$$E = E_0 e^{-rt},$$

where E_0 is the initial value of the potential, and $r = \frac{1}{RK}$, and graphically by curve A in Figure 3. Furthermore, since the period of the spark is approximately equal to the time required for the Kerr potential to fall to 36.8% of its original value, there will occur approximately two half oscillations of the spark in that time, and, represented on the same scale of abscissae, curve B, figure 3, may represent the variation of the intensity of the spark.

Now the angle through which the Nicol N_2 must be rotated to obtain equality of the images, as previously described, is shown by Mascart* to be proportional to the difference between the two refractive

* Mascart. Optique t II, p. 66

indices of the nitrobenzene when subjected to the electrostatic field. Experiment and theory with reference to the Kerr effect lead to the fact that this difference of the refractive indices is proportional to the square of the potential, i.e. to E^2 .

Therefore the restorative power of the cell, as measured by the angle α through which N_2 must be rotated, is proportional to the square of the potential.

This was verified experimentally by viewing the images of a continuously illuminated slit through two crossed Nicols, the Kerr cell and double image prism arranged exactly as in Figure 1, this time, however, applying a direct potential to the plates of the Kerr cell. Then the potential was varied in steps and the resulting variation of the angle through which the second Nicol N_2 had to be rotated to produce equality of the images, was observed. The curve in Figure 4 shows this variation. The logarithm of the potential E was plotted as ordinates with the logarithm of the angle 2α as abscissae and the straight line with slope 2.08 in Figure 5 was obtained.

The instantaneous restorative power of the Kerr cell $\alpha = \frac{1}{2}E^2 - \frac{1}{2}E_0^2 e^{-2}$, may therefore be represented by the curve C in Figure 3. If the restorative power were constant, the restored image would vary in intensity with the light from the spark as given by curve B. The angle through which the Nicol N_2 must be turned to obtain equality of the images would, in this case, be constant regardless of this variation of light intensity. The light from the spark may therefore be considered as having some constant value, the average of the ordinates

of curve ¹⁰, and lasting during the interval t_1 to t_2 , where t_1 is the instant the Kerr cell begins to discharge, and t_2 is the instant when the restorative power of the Kerr cell has fallen to a value negligible in comparison with that at the instant when the Kerr condenser begins to discharge. This is based on the assumption that the spark continues to oscillate until or after the instant t_2 just described.

Actually the restorative power of the cell has fallen to about one percent of its original value in 7×10^{-7} seconds after the Kerr cell begins its discharge. The period of the spark, on the other hand, is approximately 1.2×10^{-7} second and the photographs of the sparks showed as many as seven or eight in a series. Hence the spark continues its oscillation for at least 4×10^{-7} second, and the above assumption was justifiable.

If, however, instead of being constant, the restorative power, α , vary as in curve C, figure 3, the intensity of the restored image varies accordingly, and the angle which the eye accepts as giving equality of the images is an average value of the ordinates of curve C. This

average value of α : $\alpha_{av} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \alpha dt = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} E_0^2 e^{-2\alpha t} dt.$

$$\alpha_{av} = \frac{1}{t_2 - t_1} \frac{E_0^2}{2\alpha} (e^{-2\alpha t_1} - e^{-2\alpha t_2}).$$

But t_2 is the value of t when the potential E is negligible in comparison with its original value $E e^{-\alpha t}$, consequently $e^{-2\alpha t_2}$ may be neglected in obtaining α_{av} , and

$$\alpha_{av} = \frac{1}{t_2 - t_1} - \frac{\frac{1}{2} \frac{R_0^2}{R}}{e^{-2 \cdot t_1}}$$

Actually t_1 is the instant when the light from the spark begins to pass through the Kerr cell. Reflecting the light in a mirror and thus increasing its path varies this instant t_1 . In other words, reflecting the light in a distant mirror has the effect of moving curve B along the time axis by an amount equal to that required for the light to travel twice the distance from the spark to the mirror. Furthermore, t_2 is a constant for any one value of the resistance R, hence the average value of the restorative power of the Kerr cell, i.e. the angle through which the Nicol N_2 must be turned to obtain equality of the images varies with t, i.e. with the position of the mirror, only.

If the light illuminating the slit be that from some fluorescent substance placed very close to the spark, the light from the latter being completely hidden from the observer's view, the fluorescent light will be much fainter, but oscillatory in its intensity just as the spark light is oscillatory. And if the fluorescent substance begins to emit light the instant the light of the spark falls upon it, the angle α will be the same as that obtained when the spark itself was viewed directly. If, however, an interval of time elapses between the instant the spark light begins to fall on the fluorescent substance, and that at which the latter begins to emit light, the effect will be the same as if the two processes occurred simultaneously, but the fluorescent light were reflected in a distant mirror before it reached the Kerr cell.

It may seem at first sight that the most ideal conditions for the measurement of time intervals as short as that required for light to travel fifteen meters or less, i.e. 5×10^{-8} second, are those obtained when the resistance R in series with the Kerr cell is zero. Then, since the capacities of the Kerr cell and auxiliary condenser are approximately the same, and the inductances of their respective circuits are likewise approximately the same, the K-P circuit should oscillate with the same frequency as that of the A-P circuit. Under these conditions, however, no noticeable variation in the position of the Nicol N_2 for equality of the images was realized as the light path was increased. The reason for this is evident from the following: In as much as the position of N_2 for equality of the images is independent of the intensity of the light, the oscillatory nature of the light source has the same effect as would a light source of some average but constant intensity. The position of N_2 which would give equal intensity of the images does vary periodically, however, the period being twice that of the K-P circuit. The eye cannot follow these rapid oscillations but chooses some average position which is practically independent of the position of the mirror, at least for those positions within fifty meters from the spark. Of course it would be possible to find a position of the mirror for which the first light of the series of sparks would not reach the Kerr cell until after the last oscillation of the latter had died away and the cell would consequently not restore the light. This position would depend upon the number of sparks on the average, that were in any one series. And for positions of the mirror

just a few meters nearer to the spark P, the average position of A_2 for equality of the images as chosen by the eye would be small and would increase gradually, but would soon reach a maximum, which would persist as the mirror were brought nearer.

The arrangement shown in figure 1 may, therefore, be employed to measure the time interval between the absorption and emission of light in fluorescence by merely illuminating the fluorescent substance directly by the spark and determining the corresponding angle α for the former. Comparing this with the different values of α obtained for the various positions of the mirror it is possible to find one position of the mirror for which the value α is the same as for the fluorescent substance. In fact it is only necessary to find a point on the curve whose abscissa is the value of α obtained for the fluorescent substance. Its ordinate is the corresponding position of the mirror measured from the spark, and the time required for light to travel twice this distance is the period of time the exciting light of the spark is imprisoned within the fluorescent substance.

Method.

The experiment was first tried with the condenser plates immersed in carbon bisulphide, but the Kerr effect is not sufficiently pronounced in this case to give good results. In fact the light coming directly from the spark was only faintly restored. Nitrobenzene was then tried and two sources of difficulty at first retarded the progress

of the work. The best nitrobenzene available was found to be so conducting that no spark could be obtained. Furthermore the liquid was quite yellow and absorbed much of the light passing through it, a difficulty which assumes considerable proportions when the light is as faint as that emitted from barium platino-cyanide. This difficulty was eliminated by distilling the nitrobenzene at five millimeters pressure, a specially constructed vigoral column being employed during the process. At this pressure the nitrobenzene boiled at about 90° centigrade, and the condensing liquid became gradually paler in color as the distillation proceeded. The middle section which was a pale straw color was selected and found to absorb only a negligible quantity of light. It also served well as a dielectric/^{but} was further improved by applying a constant voltage of about 250 volts for ten or twelve hours to the terminals of the Kerr cell.

The electrical connections were so arranged that when the Kerr cell was not needed in the circuit of the spark gap, the direct voltage of 250 volts was applied to the cell. The resistance of the latter was found to increase from 70000 ohms to several megohms by merely applying the constant voltage for about twelve hours. The resistance remained practically the same for two hours after disconnecting the cell from the source of potential. The constant potential was applied to the cell always in the same direction. The Kerr effect of the cell was strongest immediately after disconnecting it from the source of constant potential and decreased slightly during a minute after which

it remained constant. In determining the angles for any one position of the mirror M, a series of settings of the analysing Nicol were made alternately on the two sides of the zero position, the successive readings on the same side of the zero position agreeing by one degree or less being taken as an indication that the Kerr effect of the cell was constant. This was realized usually after the first setting was made. The settings of the analysing Nicol for equality of the images were accurate to within a half degree; often the successive readings agreed even more closely.

The method of determining the dark time of any fluorescent substance employed in the present work is to determine the rate at which the restoration of the Kerr cell decreases with some high resistance as a thousand or fifteen hundred ohms as the damping resistance R, and to determine the difference between the angle 2α for the fluorescent substance in question and that obtained by viewing the spark directly under the same conditions. If this difference is large, say five to ten degrees, evidently the period of darkness for this substance is long, for with such a high resistance in the circuit described above, the angle 2α varies by about five degrees as the mirror M is moved from the spark to a position forty-five meters from the spark. For a case of this kind results obtained when R is two hundred ohms or less are not reliable since for such a low resistance the restoration decreases almost to zero in the time required for light to travel ninety meters*, and the cell would consequently only

* See curve E.

slightly restore the fluorescent light, thus making it difficult if not impossible to balance the intensities of the two images. In such a case the resistance should be kept as large as four hundred ohms or more and the fluorescent light would be restored accordingly.*

If, however, with a thousand ohms in the circuit the angle 2γ for the fluorescent substance examined differs by only a degree or two from the angle obtained from observations made directly on the spark, the time interval in question is of the order of magnitude of that required for light to pass twice the distance from the spark to a mirror about twenty meters away. In such a case lower resistance must be employed so as to increase the rate of decay of charge on the plates of the Kerr cell and thus increase the rate of change of the restoration of the cell.

The shape of the curves obtained showing this rate of change of restoration, i.e. the restoration expressed in terms of the angle 2γ as a function of the distance between the spark and mirror, depends, in an electrical arrangement shown in figure 1, not alone upon the resistance R, but also upon the width of the spark gap. Curves A, B, D, which were taken with a spark gap of approximately one centimeter, show oscillations. When the spark gap was reduced to two or three millimeters curves such as 1, figure 2, were obtained. In instances where the dark time is very short these oscillations are highly

*See Curve C.

undesirable, for there are two and sometimes three points on the curve whose abscissae are the same angle 2α as obtained for the fluorescent substance. If, however, the resistance is changed, and another curve and angle 2α for the fluorescent substance determined, there will again be two or three points on this new curve whose abscissae equal the new angle 2α for the fluorescent substance. One of these points only, however, will have the same ordinate as one of the three points of the preceding curve. So that, even if the oscillations exist, it is still possible to determine a short time interval.

The method, therefore, is to determine approximately the interval with a high resistance R in the electrical circuit, and then more accurately with a lower resistance if necessary. The best conditions are obtained when the nature of the resulting curve is such as to have a rapid change in 2α in the region of the angle of the fluorescent substance, but at the same time the latter angle should be not only fairly large, which is consistent with brightness of the restored images, but should also differ by ten or fifteen degrees from the angle obtained when viewing the spark directly; then the error in the determination of 2α for the fluorescent material has a relatively small error in the dark time.

Results.

Five determinations of the time interval between the absorption and emission of light in the case of barium platino cyanide were made, using four different resistances varying from two hundred to four hundred

ohms. Curves A,B,C,D,E in figure 6 show the results. The abscissae of curve C are diminished by forty degrees to avoid crowding the curves. The following table gives the angle obtained for barium platino cyanide in each case and the corresponding position of the mirror which would give the same angle as taken from the curve. Twice the average of these distances when divided by the velocity of light gives the dark interval for barium platino cyanide.

Curve	R ohms	Angle	Distance cm.
A	300	48 ⁰ .7	3180
B	250	53.2	3196
D	300	54.1	3180
E	200	40.6	3158

Mean "a" = 3181 cm.

$$T = \frac{2a}{v} = \frac{2.3181}{3 \times 10^{10}} = (2.12 \pm .01) \times 10^{-7} \text{ sec.}$$

Table 1.

The value of "a" obtained from Curve C, although agreeing as well as could have been expected with the other values, was not used in calculating the mean, for in this case the resistance was four hundred ohms and the curve so steep that a variation of half a degree in the angle resulted in a variation of seventy-five centimeters in the distance "a". The maximum deviation from the mean value is fifteen parts in 3181 or about half of one percent. The time interval calculated from this is $(2.12 \pm .01) \times 10^{-7}$ second, or about one five millionth of a second.

The next substance examined was rhodamine in a solution of acetone, acetic acid and glycerine. While fresh from the bottle in which the solution was kept it showed a short but very distinct interval between the absorption and emission of light. If allowed to remain for fifteen or thirty minutes in the air the sample became hard and dry and then the Kerr cell restored its fluorescent light equally as well as it restored the light of the spark. It evidently became phosphorescent so that the light excited by the passage of one spark continued even to the next spark; in other words, the duration of phosphorescence was as long or longer than the interval between sparks. The latter was approximately one twentieth of a second. All observations on rhodamine were therefore made within five minutes after the sample was taken from the container.

The fluorescence of rhodamine was bright red and no difficulty was experienced in matching the intensities of the two images. The accuracy in this case was, however, not as good as in the case of barium platino cyanide. The slope of the curves in the region of the point corresponding to rhodamine was practically the same as in the case of barium platino cyanide, and the images could be matched with the same but no greater precision in either case, so that as far as these features are involved the accuracy should be about the same in the two cases. As a matter of fact out of seven determinations of the interval of dark time of rhodamine with values for R covering a range from eighty to two hundred ohms, the maximum deviation from the mean value of " α " is twenty two centimeters. It was fifteen centimeters

in the case of barium platino cyanide. If, therefore, the time interval were the same in the two cases, the percent error would be approximately the same, but as may be seen from table 2 the distance " " for rhodamine is 316 centimeters, about one tenth that for barium platino cyanide, and the accuracy is accordingly less. The mean value 316 centimeters for " " yields $(2.11 \pm .14) \times 10^{-8}$ second as the period of dark time for rhodamine.

Curve	R ohms	Angle	Distance cm.
F	200	53 ⁰ .5	325
A'	150	59 .0	313
B'	200	54 .0	320
C'	100	62. 0	303
D'	80	37. 3	302
E'	80	47. 9	238
F'	80	43. 3	312

Mean " " = 316 cm.

$$T = \frac{2t}{v} = \frac{2.316}{3.10^{10}} = (2.11 \pm .14) \times 10^{-8} \text{ sec.}$$

Table 2.

The curves obtained in determining the time interval for rhodamine are shown in figure 7. Curve B' is there drawn to the same scale of abscissae as the other curves in the figure but to half scale in the ordinates. The abscissae of r and F' are diminished by 20⁰ to avoid crowding the curves. Particular attention is called to A' and C' which show the oscillations referred to above. In each of these cases there are three points whose abscissae are the angle 2γ obtained from the observations made on rhodamine, the ordinate of one only, of A' is the same as the ordinate of one of the three points of C'. This ordinate, moreover, agrees well with those obtained from the curves showing no oscillations.

In conclusion the author desires to acknowledge his great indebtedness to Professor Wood, at whose suggestion the work was undertaken, and under whose supervision it was carried out. He also wishes to thank Professor Ames for his interest and valuable suggestions during the progress of the work, and also to Dr. Frank V. Grimm, who prepared the nitrobenzene.

DIAGRAM OF APPARATUS

Fig 1

Fig 2.

Fig. 3.

Fig. 2

Fig. 6

Fig 7

Biographical Note.

Philip Frederick Gottling, son of Bernhard F. and Mattie Gottling, was born in Baltimore, Maryland on the 7th of December 1897. He received his preparatory education at the Baltimore City College, graduating in 1915. In the same year he entered the School of Engineering of the Johns Hopkins University and received the degree of Bachelor of Engineering in 1919. He then entered the Physical Department of the graduate school, holding a Scholarship in that department for the year 1919-1920, and taking courses under Professor Ames and Associate Professor Ifund in Physics, and Professors Cohen and Murnaghan in Mathematics.

The following year he held a position as student engineer at the General Electric Company, Schenectady, New York. He again held a scholarship in the Physics Department of the Johns Hopkins University during the years 1921-22 and 1922-23, attending lectures by Professors Ames and Wood in Physics and Professor Murnaghan in Mathematics. He received the degree of Master of Arts in June 1922.